Na_{1+x}Al_xGe_{2-x}P₃O₁₂ (x = 0.5) glass-ceramic as a solid ionic conductor for sodium ion

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Abstract

Sodium-ion conducting glass-ceramics composed of Na_{1+x}Al_xGe_{2-x}P₃O₁₂ (x = 0.5) crystalline conducting phase were successfully prepared by heat-treating the parent glass at different temperature and time, and were characterized with DSC, XRD, CV, SEM and alternative current impedance. The relationship between the ionic conductivity and crystallization conditions (time and temperature) of the sodium aluminum germanium phosphate (NAGP) glass-ceramic was investigated. Results show that the NASICON phases containing Al³⁺ in all these glass-ceramics are isomorphous with NaGe₂P₃O₁₂ and stable against sodium metal. The highest total conductivity of the glass-ceramic material, 9.27×10⁻⁵ S cm⁻¹ at 140 °C, is obtained by highly crystallizing the glass at 750 °C for 12 h. The reasons for the enhancement of the ionic conductivity in the glass-ceramics are discussed in view of the dependence of microstructure morphology on the heating condition. It could be attributed to its good crystallization of the conductive phase NAGP, uniform grain size and possible optimizing conductive pathway of Na⁺ ions.

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1. Introduction

Sodium-ion batteries (NIBs) have attracted great attentions particularly in electric vehicles (EVs) and large scale electrochemical storage for biomass, solar radiation, wind and waves and so on because of the huge abundant sodium resources, low cost (Na₂CO₃ 0.07-0.37 € kg⁻¹ vs. Li₂CO₃ 4.11-4.49 € kg⁻¹) and very suitable redox potential ($E^o_{(Na^+/Na)} = 2.71$ V versus standard hydrogen electrode; only 0.3 V above that of lithium) [1-7]. The very high reactivity of sodium with moisture and oxygen, the quest for safer and more reliable electrolyte systems is therefore urgent, and solid electrolytes (SEs) are promising candidates in this regard [8-10].

However, most polymer electrolytes coupling a polymer with a plasticizing organic solvent for NIBs still present some drawbacks [11,12]. In this respect, inorganic solid electrolytes (solid sodium ion conductors) present potential advantages like a large electrochemical stability window, highly thermal stability, absence of leakage and pollution, a high resistance to shocks and vibrations and the possibility of easy miniaturization [13, 14]. One prominent example of the solid Na⁺ ion conductor is Na-β"-Al₂O₃ that is mostly used in the high temperature sodium batteries (sodium-sulfur batteries) as an electrolyte with an ionic conductivity of 0.2 ~ 0.4 S cm⁻¹ at 300 °C [4]. Another extensively studied Na⁺-conducting solid electrolytes are NASICON (Natrium (Na) Super (S) Ionic (I) Conductor (C)), general formula is AM'M''P₃O₁₂) type compounds which demonstrate sodium ionic conductivity in a three-dimensional frameworks (any crystallographic

direction) in comparison with Na- β -Al₂O₃ (layer structure), which possesses only two-dimensional Na⁺ mobility [15, 16]. Solid solutions of Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (NZSP, 0 ≤ x ≤ 3), firstly reported by Hong and Goodenough [17, 18], are typical examples of NASICON-type compounds which are characterized by relatively large ionic conductivities in the order of 10⁻¹ S cm⁻¹ at 300 °C and 10⁻⁴ S cm⁻¹ at ambient temperature [8, 19]. Hence, the properties of the chemically stable Na⁺-conducting SEs with high sodium-conductivity at room temperature, good cation-exchange with electrode materials and so on should make them possible for application in room temperature all-solid-state NIBs with high safety [20].

However, high porosity and big grain boundary as well as the difficulties in obtaining the desired shapes of the sintered NASICON-type ion conductors affect their practical applications as SEs in NIBs [21]. Compared to the sintered materials, glass-ceramics can be made into desired shape and size more easily because of their pore-free and small grain size [22]. So far, few reports were dedicated to sodium ionic conductors with NASICON-type structure containing Al cations, let alone the glass-ceramics with same composition. Only Li⁺-conducting glass-ceramics composed with crystalline containing Al³⁺ NASICON phase have been reported [11]. Due to the close ionic radius of Al³⁺ compared to that of Ge⁴⁺, the Al cation is likely within the tolerability limit of NaGe₂(PO₄)₃ framework. Furthermore, during the ceramic synthesis of these compounds, ALPO (aluminum phosphate) side-compounds can be easily formed. Phases such as berlinite (ALPO), with tetrahedral PO₄³⁻ groups, are very stable. Once formed they do not react to yield desired NASICON-type products [23-25].

In this study, we report sodium ion conducting glass-ceramics containing crystalline NASICON phase, Na_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂, and its preparation method. Al³⁺ in the glass-ceramics

entered the structure of NASICON and partly substituted the Ge^{4+} . Sodium ionic conductivity of the solid electrolyte is up to $9.27 \times 10^{-5} \text{ S cm}^{-1}$ at 140 °C. Meanwhile, the effects of crystallization time and temperature on the ionic conductivity of the glass-ceramic have also been investigated. The prepared ion conductor extends the family of the $\text{Na}_{1+x}\text{Al}_x\text{Ge}_{2-x}\text{P}_3\text{O}_{12}$ system and provides great promise for practical application in room-temperature sodium ion batteries or chemical sensors.

2. Experimental

A glass batch of $[18.75\text{Na}_2\text{O} \cdot 6.25\text{Al}_2\text{O}_3 \cdot 37.50\text{GeO}_2 \cdot 37.50\text{P}_2\text{O}_5 \text{ (mol \%)}]$ was prepared by using reagent-grade chemicals such as Na_2CO_3 (Sinopharm, China), Al_2O_3 (Sinopharm, China, particle size <10 μm), GeO_2 (Sinopharm, China) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Sinopharm, China). The aforementioned chemicals were weighed, mixed, and ground for 10 min in an agate mortar. For further homogenization, the batch was milled in a glass jar for 1 h by using a ball mill. The milled batch was melted in a platinum crucible at high temperature (1350 °C) for 2 h to get a clear, homogeneous and viscous melt, which was poured onto a preheated (250 °C) stainless steel (SS) plate at room temperature and pressed by another SS plate to yield transparent NAGP glass sheets (thickness: $\sim 200 \mu\text{m}$). Subsequently, the pressed glass sheets were crystallized at different temperatures to release the thermal stresses and then cooled to room temperature to give $\text{Na}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ (NAGP) glass-ceramics.

Except stated, the following measurements were performed at room temperature. Thermal characterization of NAGP glass-ceramic samples was carried out using differential scanning calorimetry (DSC) in the nitrogen by Perkin-Elmer TGA7/DSC7 from room temperature to 800 °C at the rate of $10 \text{ }^\circ\text{C min}^{-1}$. Based on the DSC data, thermal treatment was done in two steps. In the

first step, the samples were heated to the temperature between glass transition temperature (T_g) and crystallization temperature (T_c) for 2 h in order to form the crystal nucleus. In the second step, the glassy samples were heated at the temperatures above T_c for different periods to reach the best treating conditions to optimize the conductivity of the glass ceramics. The heating and cooling rates for the crystallization were 3 °C min⁻¹. The crystallization process transformed the glass to glass-ceramic, which led to a change in the appearance of the glass from colorless transparent to grayish opaque. Elemental components were obtained from the analysis by using a Thermo E. IRIS Duo inductively coupled plasma atomic absorption spectrometer (ICP-AAS). X-ray diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer (50 KV, 50 mA) with a copper target ($\lambda = 1.5405 \text{ \AA}$) and Ni filter at a scan rate of 5 ° min⁻¹ from 10° to 80°. The surface morphology of the fractured and thermally annealed samples were investigated by Philips XL30 scan electron microscopy (SEM). All of the samples were sputtered with gold prior to the SEM measurement. The thickness of the membranes was measured with a micrometer (SM & CTW, Shanghai).

The ionic conductivities were measured by electrochemical impedance spectroscopy (EIS). A gold coating of 0.5 μm thickness was sputtered on both sides of these samples before measurement. The samples were measured in blocking-type cells where the gold-coated solid membranes were sandwiched between two stainless steel electrodes ($\Phi = 18 \text{ mm}$). Impedance data were obtained with an electrochemical working station CHI660C (Chenhua) in the frequency range 1 Hz - 100 kHz between 20 °C and 140 °C. At each temperature, the sample was equilibrated for 1 h prior to the impedance measurement. The ionic conductivity was calculated from the equation (1):

$$\sigma = l / (R_b A) \text{ (S cm}^{-1}\text{)} \quad (1)$$

where σ is the ionic conductivity, R_b is the total electrolyte resistance (including both bulk and interfacial contributions) from EIS, l is the thickness of the solid electrolytes, and A is the area of the stainless steel electrode since the area of inorganic membrane is larger than that of the steel electrode.

The electrochemical stability of the glass-ceramic samples was determined from the linear sweep voltammogram by the electrochemical working station CHI660C (Chenhua) using a two-electrode cell. Stainless steel was used as the working electrode and sodium foil as the counter and reference electrode. The measurement was done between 0 and 5.5 V (vs. Na^+/Na) at the scan rate of 1 mV s^{-1} .

3. Results and Discussion

The DSC curve of the glass batch NAGP from room temperature to 800°C is shown in Fig. 1. The sample presents an inflection at 565°C , which is related to the glass transition temperature (T_g). An exothermic peak (T_c) at 635°C is attributed to the crystallization of the glass during its conversion to glass–ceramic. It should be noted that some crystallization does occur in the glass even before T_c , but at T_c rapid crystallization of the glassy matrix takes place. At this temperature range only one sharp peak was observed, indicating the formation of single crystalline phase. Based on the DSC data, the samples were heated to 600°C for 2 h and then subsequently crystallized at 700°C , 750°C , 800°C , and 850°C for 12 h, separately. Another two samples were crystallized at 750°C for 8 and 24 h.

The ICP analysis data for the sample from heat-treatment at 850°C show that the component is $\text{Na}_{1.49}\text{Al}_{0.50}\text{Ge}_{1.499}\text{P}_{2.99}\text{O}_{12}$, and the relative error is about 5%. It is almost consistent with the

ratio for the precursors. Although some elements would evaporate during the heat-treatment at the high temperature up to 850 °C, the evaporated content is not much.

The XRD patterns of $\text{Na}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ glass-ceramics are shown in Fig. 2. It was observed that almost no impure phase can be detected. The XRD peaks coincided well with the data of JCPDS 33-1245 ($\text{NaGe}_2\text{P}_3\text{O}_{12}$), confirming the formation of a single crystallization phase indexed to rhombohedral NASICON-type structure. Therefore, it could be inferred that the added Al^{3+} ions entered the structure of $\text{NaGe}_2\text{P}_3\text{O}_{12}$ by replacing Ge^{4+} ions. The prepared glass-ceramics containing NASICON phase consists of crystal phase and amorphous region. So the exact number of Al^{3+} entering the NASICON structure needs to be tested further in the future if possible convenient measurement is available. These results also indicate that NASICON-type $\text{Na}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ is the major conductive crystal phase in the glass-ceramics.

SEM micrographs of the surfaces for the $\text{Na}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ glass-ceramics membranes crystallized under different conditions are shown in Fig. 3. Generally, all of the glass-ceramic samples possess a very dense microstructure without any pores and cracks. Furthermore, it is observed that the contact among grains is very close. Evidently, notable differences in the fracture microstructure are observed. The grains of the sample crystallized at 750 °C for 8 h are very small in size (about 200 nm) and irregular in shape (Fig. 3a). As the crystallization time increases to 12 h, the grains and grain boundaries become distinct. The existence of mostly cube-shaped grains with size in the 300 - 500 nm range is evident (Fig. 3b). An increase in grain size with an increase in the crystallization time from 12 h to 24 h is apparent. A wide distribution of grain shape and size is observed in the sample crystallized at 750 °C for 24 h (Fig. 3c). As shown in Fig. 3d, the glass phase glass-ceramic sample crystallized at 700 °C is apparent though the grains began to

appear. As the crystallization temperature increases to 800 °C or 850 °C, the melting phenomenon takes place, which is more obvious for the sample from the heat-treatment at higher temperature (Fig. 3f).

The alternative current impedance spectra for the NAGP glass-ceramic samples treated at different temperatures for 12 h at 140 °C are shown in Fig. 4. Only one distorted semicircle is observed in the spectra of all samples. The total resistances of the samples were therefore obtained from the right intercepts of the semicircle with the real axis in the spectra. The total resistance, R_b , is used to calculate the corresponding conductivity values of σ . Obviously, the total resistance for the NAGP glass ceramics noticeably changes with the treatment temperature. It can be seen clearly that R_b decreases when the temperature increases from 700 to 750 °C, and then increases with further increase of the temperature. As the crystallization temperature increases, the total conductivity, σ , starts from $1.03 \times 10^{-5} \text{ S cm}^{-1}$ and peaks ($9.27 \times 10^{-5} \text{ S cm}^{-1}$) at 750 °C; then it decreases to $4.30 \times 10^{-5} \text{ S cm}^{-1}$ and $2.12 \times 10^{-7} \text{ S cm}^{-1}$ as the crystallization temperature increases to 800 and 850 °C, respectively.

The Arrhenius plots of total ionic conductivity, σ , in the 20 to 140 °C temperature range for the samples crystallized for different time (8, 12 and 24 h) at 750 °C are shown in Fig. 5. The ionic conductivity increases with the test temperature. It is due to the increase in the thermally activated mobility of ions according to the hopping conduction mechanism. The conductivity data are all found to be linear and fit well with the Arrhenius equation Eq. (2):

$$\sigma = A \exp (-E_a / kT) \quad (2)$$

where A is the pre-exponential factor, T the absolute temperature, E_a the conduction activation energy, σ the conductivity and k the Boltzmann constant, respectively. The results illustrate that

there is no structure or phase change for all samples in the tested temperature range because there are no turning points on the curves. The activation energy (E_a) for the thermally activation hopping process was obtained by a linear regression fitting the conductivity data with Arrhenius equation. From the slopes of the straight lines in Fig. 5, the activation energies (E_a) for mobile ions were calculated. The details of total ionic conductivity and activation energies of those samples are summarized in Table 1. The sample crystallized at 12 h presents the highest ionic conductivity in the entire temperature range. The lowest activation energy of 0.53 eV was obtained at 12 h for NAGP glass-ceramics treated at 750 °C. It is concluded from the SEM observations that the migration of Na^+ ions is favored by the formation of crystalline grains with NASICON-type network structure and dense microstructure. Closer contact favors the migration of Na^+ ions at the grain boundary and leads to higher ionic conductivity. The very high ionic conductivity and low E_a of the sample treated at 750 °C for 12 h could be attributed to its good crystallization of the conductive NAGP phase and uniform grain size. Of course, similar to other solid electrolytes such as $\text{Li}_2\text{O-B}_2\text{O}_3\text{-P}_2\text{O}_5$ [26], the pathways for Na^+ ions may be changed with the temperature leading to the change of ionic conductivity.

The electrochemical stability range of the glass-ceramic sample was determined by linear sweep voltammogram through the system stainless steel/NAGP/Na, which is presented in Fig. 6. It can be seen from the result that the glass-ceramic sample does not decompose at the potential range of 0~5.5 V *versus* Na/Na⁺. It is obvious that the NAGP has an excellent electrochemical stability as a sodium ion conductor. This suggests that the NAGP can be compatible with high-voltage electrode materials and can be used in sodium ion batteries and sodium//sulfur batteries.

4. Conclusions

Sodium ionic conducting glass-ceramic containing $\text{Na}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ as the crystalline phase has been prepared by heat-treating the parent $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{GeO}_2-\text{P}_2\text{O}_5$ -based glass. The as-prepared composition extends the family of the $\text{Na}_{1+x}\text{Al}_x\text{Ge}_{2-x}\text{P}_3\text{O}_{12}$ NASICON system. The sample treated at 750 °C for 12 h displays the highest ionic conductivity of $9.27 \times 10^{-5} \text{ S cm}^{-1}$ (140 °C) with activation energy of as low as 0.53 eV. It could be attributed to its good crystallization of the conductive phase NAGP and uniform grain size. Furthermore, the samples are electrochemically stable at 5.5 V (vs. Na/Na^+) at room temperature. The good thermal and chemical stability, easy preparation and low cost of the Na^+ -conducting glass-ceramic make it promising a candidate as electrolyte for batteries or chemical sensors.

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Captions of figures and table:

Fig. 1 DSC curve of $\text{Na}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ glass sample.

Fig. 2 XRD patterns of NAGP samples crystallized at different temperature and time.

Fig. 3 SEM micrographs of the surfaces of the glass–ceramic samples crystallized at different conditions: (a) 750 °C for 8 h; (b) 750 °C for 12 h; (c) 750 °C for 24 h; (d) 700 °C for 12 h; (e) 800 °C for 12 h; and (f) 850 °C for 12 h.

Fig. 4 Impedance plots for the NAGP glass-ceramic samples treated at different temperature for 12 h at 140 °C.

Fig. 5 Arrhenius plots of total ionic conductivity, σ_t , of glass-ceramic samples crystallized at 750 °C for 8, 12 and 24 h in the temperature range of 20-140 °C.

Fig. 6 The linear sweep voltammograms for NAGP from 0-5.5 V (vs. Na/Na^+) at 1 mV s^{-1} .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Tab. 1 Total ionic conductivity and activation energies for NAGP glass–ceramic sheets crystallized at 750 °C for different time.

Crystallization time	σ (140 °C)	σ (100 °C)	σ (20 °C)	E_a / eV
/ h	/ S cm ⁻¹	/ S cm ⁻¹	/ S cm ⁻¹	
8	2.60×10^{-5}	7.38×10^{-6}	1.47×10^{-7}	0.55
12	9.27×10^{-5}	1.31×10^{-5}	2.02×10^{-7}	0.53
24	1.35×10^{-5}	3.15×10^{-6}	1.62×10^{-8}	0.59